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(54) **SYSTEM AND METHOD FOR SENSING AND MITIGATING HYDROGEN EVOLUTION WITHIN A FLOW BATTERY SYSTEM**

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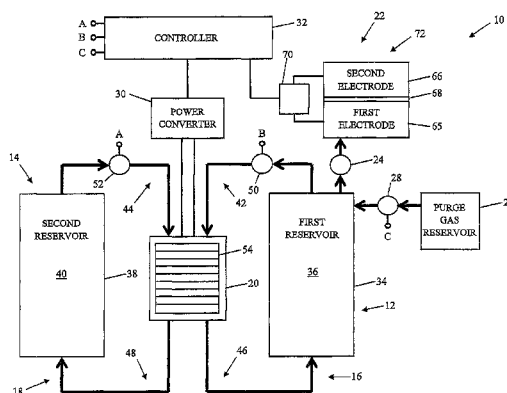*H01M 8/04* (2016.01)
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(57) **ABSTRACT**

A method is provided for mitigating hydrogen evolution within a flow battery system that includes a plurality of flow battery cells, a power converter and an electrochemical cell. The method includes providing hydrogen generated by the hydrogen evolution within the flow battery system to the electrochemical cell. A first electrical current generated by an electrochemical reaction between the hydrogen and a reactant is sensed, and the sensed current is used to control an exchange of electrical power between the flow battery cells and the power converter.

10 Claims, 4 Drawing Sheets

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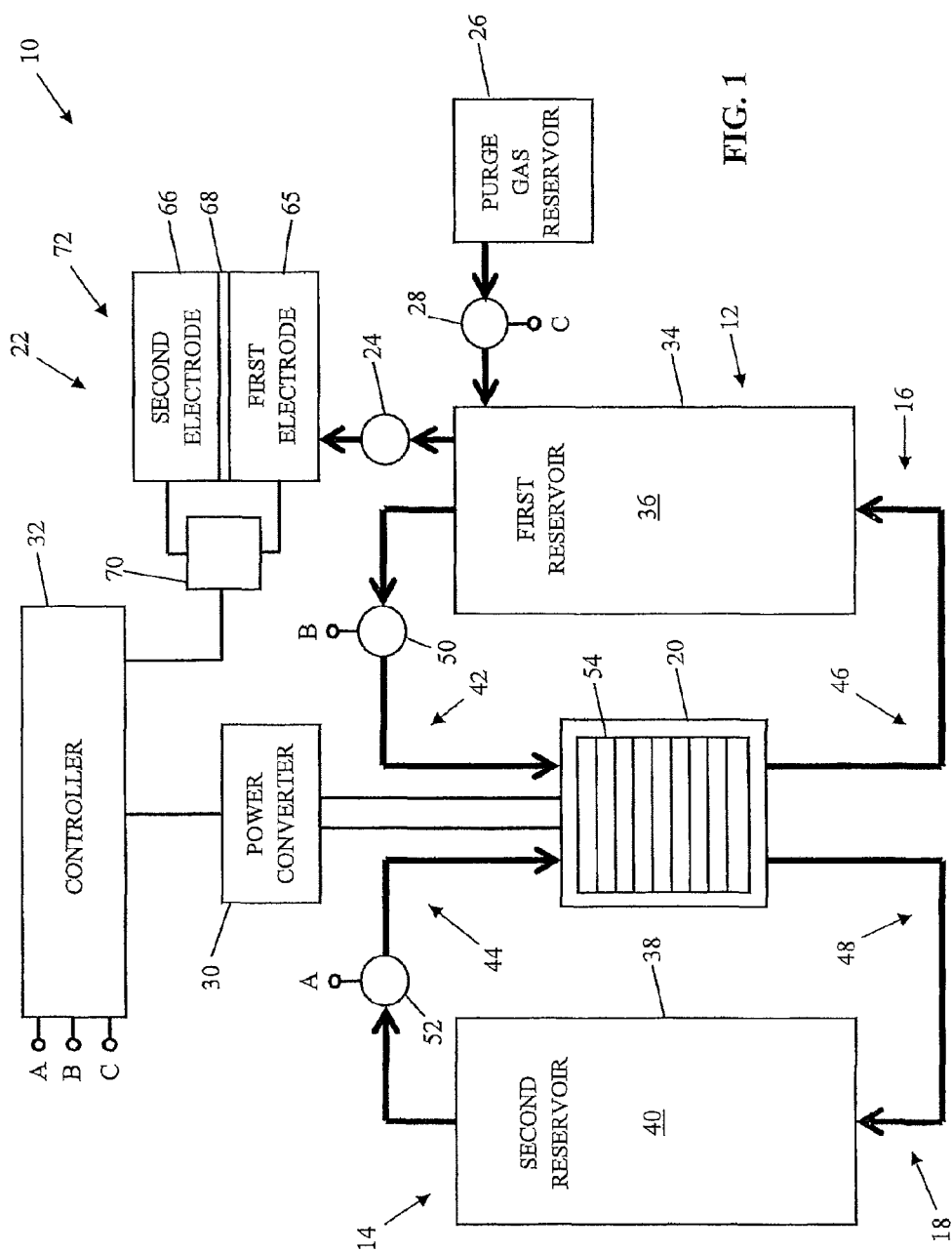Japanese office action for JP2014-517121 dated Mar. 1, 2016.
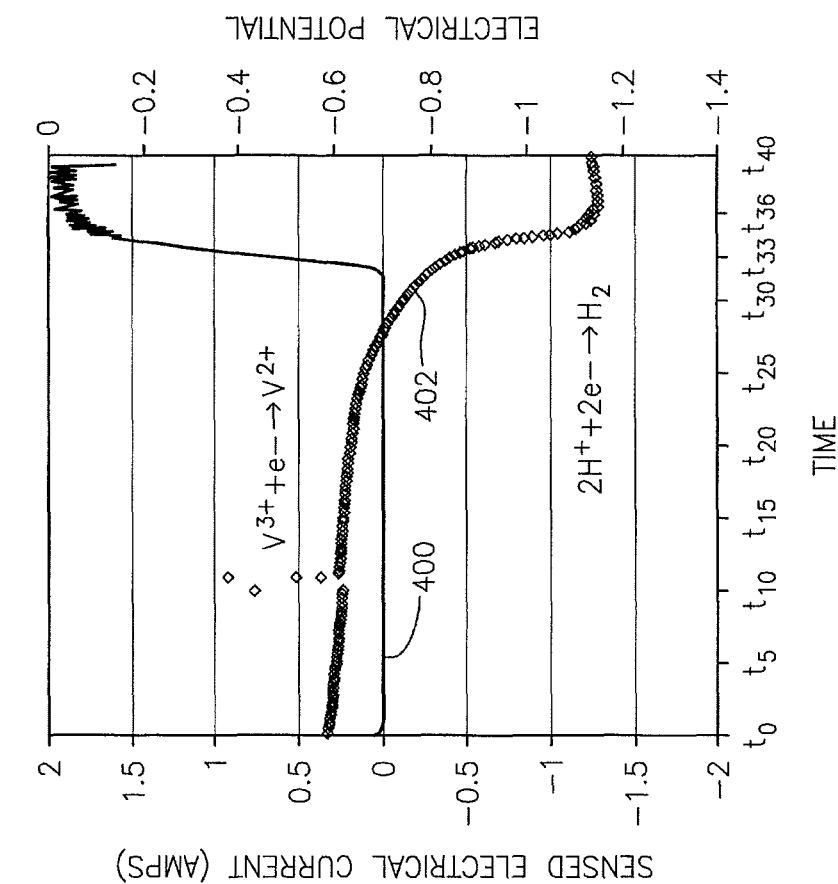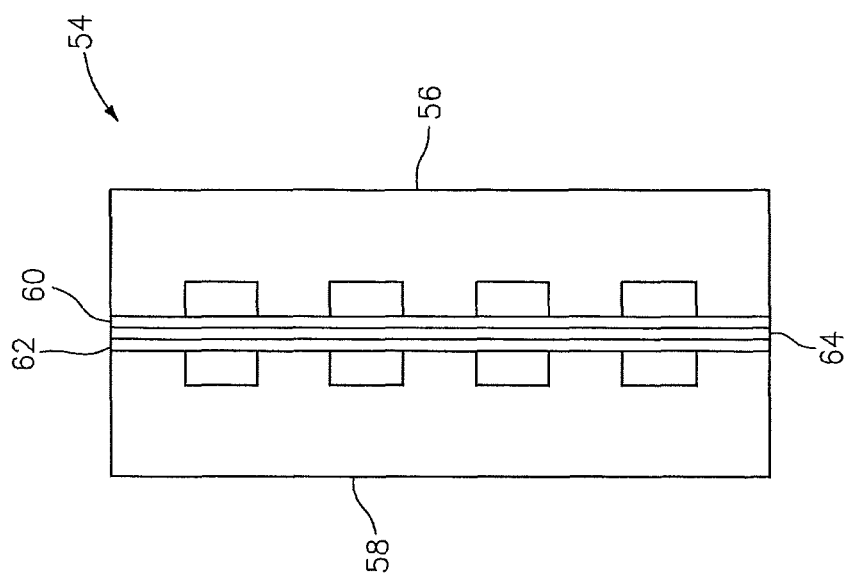
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FIG. 1

FIG. 4

FIG. 2

STEP 300
OPERATE THE FLOW BATTERY CELLS
AT A FIRST ENERGY INPUT RATE

STEP 302
INJECT PURGE GAS INTO THE FIRST RESERVOIR SUCH THAT
THE PURGE GAS AND OTHER GASES (e.g., HYDROGEN)
WITHIN THE FIRST RESERVOIR FLOW INTO
THE FIRST ELECTRODE OF THE ELECTROCHEMICAL CELL

STEP 304
PROVIDE REACTANT (e.g., AIR) TO THE SECOND ELECTRODE
OF THE ELECTROCHEMICAL CELL

STEP 306
GENERATE AN ELECTRICAL CURRENT THROUGH
AN ELECTROCHEMICAL REACTION BETWEEN
THE HYDROGEN AND THE REACTANT

STEP 308
SENSE THE ELECTRICAL CURRENT, AND
PROVIDE A CURRENT SIGNAL INDICATIVE THEREOF
TO THE CONTROLLER

STEP 310
SIGNAL THE POWER CONVERTER TO CONTROL
THE EXCHANGE OF ELECTRICAL POWER BETWEEN
THE POWER CONVERTER AND THE FLOW BATTERY CELLS
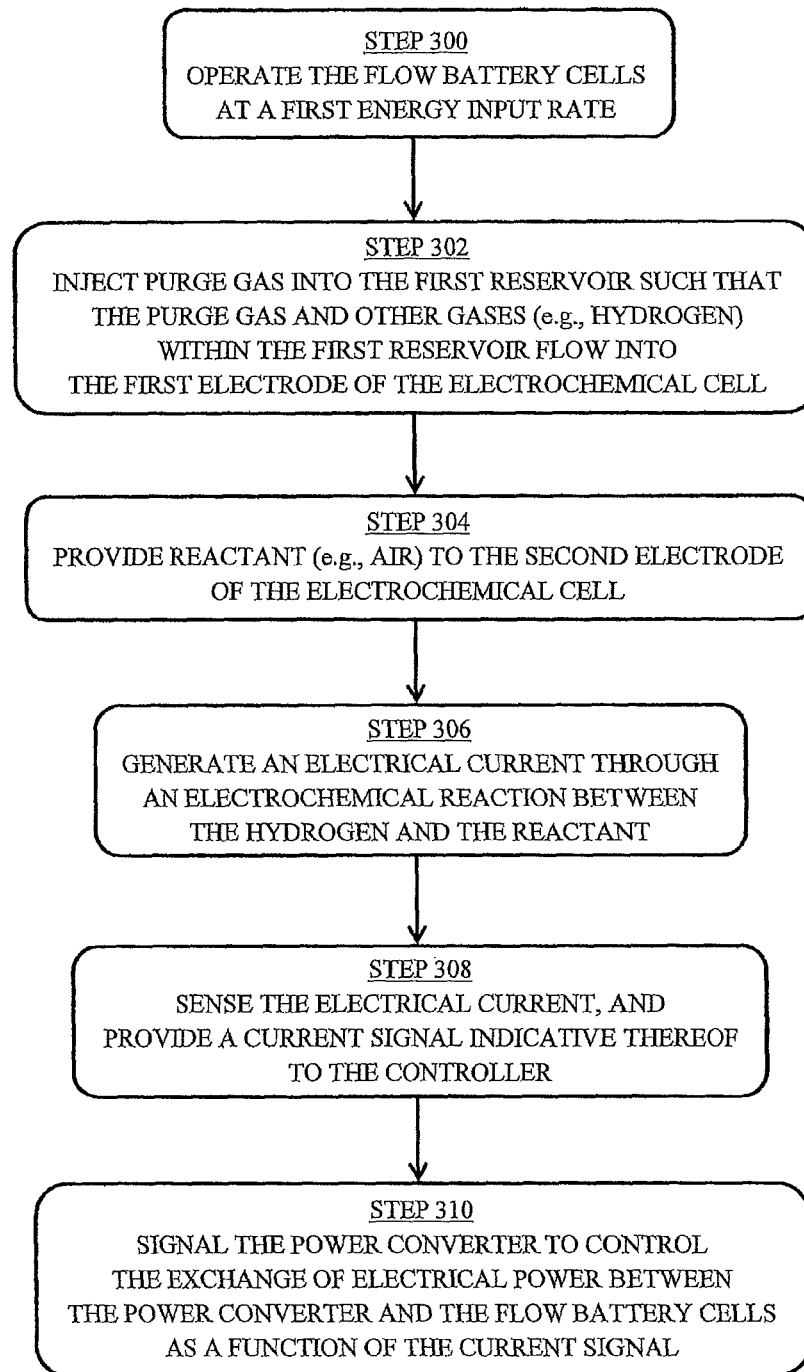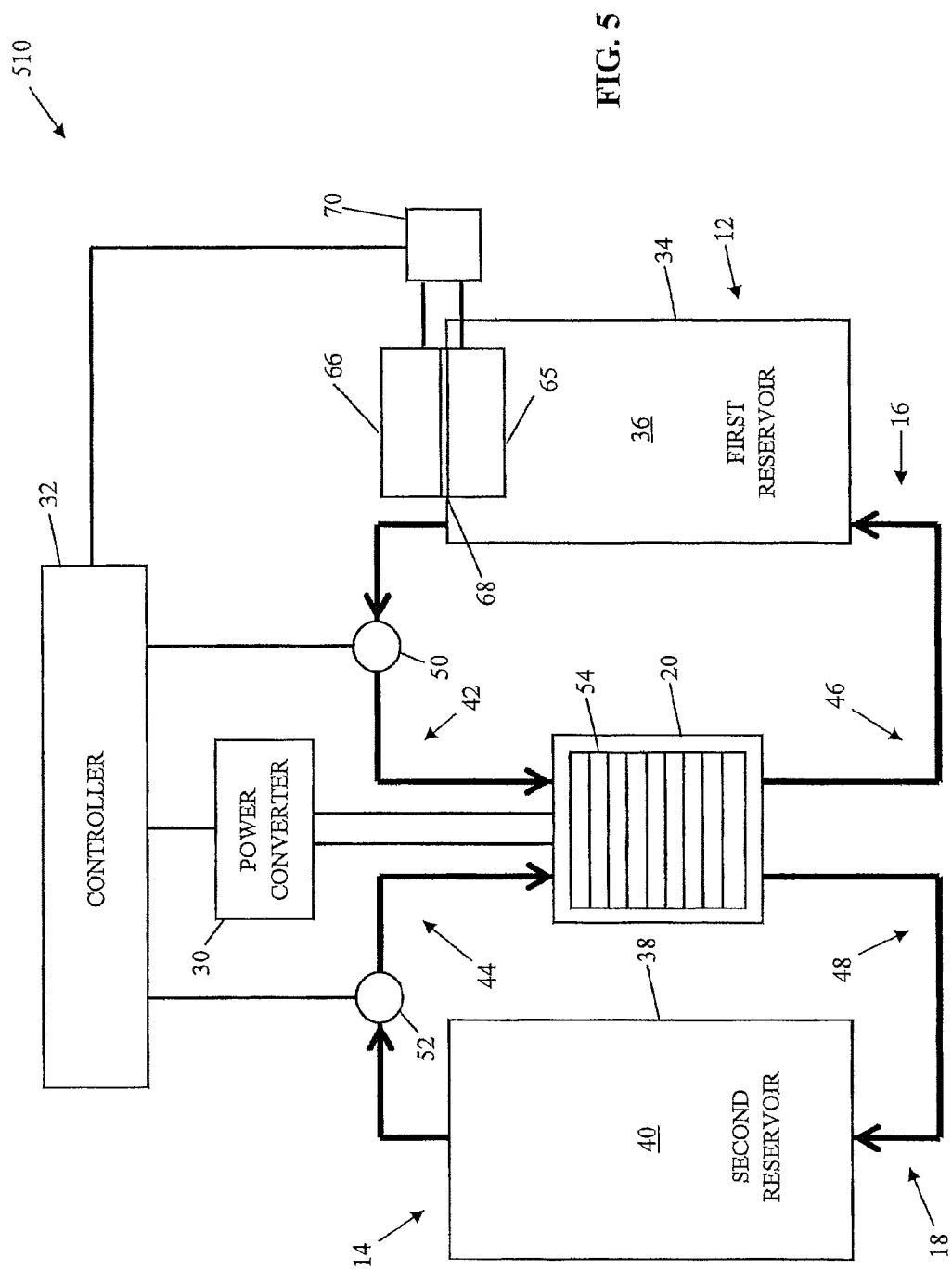AS A FUNCTION OF THE CURRENT SIGNAL

FIG. 3

FIG. 5

SYSTEM AND METHOD FOR SENSING AND MITIGATING HYDROGEN EVOLUTION WITHIN A FLOW BATTERY SYSTEM

This application is a continuation of U.S. patent application Ser. No. 13/164,059 filed Jun. 20, 2011.

BACKGROUND

1. Technical Field

This disclosure relates generally to flow batteries and, in particular, to a system and method for sensing and mitigating hydrogen evolution within a flow battery system.

2. Background Information

A typical flow battery system includes a flow battery stack, an anolyte reservoir and a catholyte reservoir. An anolyte solution is circulated between the anolyte reservoir and the flow battery stack. A catholyte solution is circulated between the catholyte reservoir and the flow battery stack.

During operation, the flow battery stack may convert electrical energy into chemical energy, and store the chemical energy in the anolyte and catholyte solutions. Hydrogen evolution within the anolyte solution, however, may also occur as the electrical energy is being converted to chemical energy. The term "hydrogen evolution" describes a secondary reaction where positively charged hydrogen ions combine with negatively charged electrons to form hydrogen gas. The formation of hydrogen within the anolyte solution may decrease system efficiency and may also create an imbalance between the states of charge of the anolyte and catholyte solutions. It also may result in unsustainable changes to the composition of the solutions, which may require these solutions to be replenished. There is a need for a system and method for sensing and mitigating hydrogen evolution within a flow battery system.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. **1** illustrates a flow battery system;

FIG. **2** illustrates a cross-section of a flow battery cell;

FIG. **3** is a flow chart illustration of steps for charging a flow battery system in a manner that mitigates hydrogen evolution;

FIG. **4** is a graphical illustration of a first curve showing sensed electrical current versus time, and a second curve showing electrical potential of a first solution versus time; and

FIG. **5** illustrates an alternative embodiment flow battery system.

DETAILED DESCRIPTION

FIG. **1** illustrates a flow battery system **10**. The flow battery system **10** includes a first reservoir **12**, a second reservoir **14**, a first solution flow circuit **16**, a second solution flow circuit **18**, a flow battery stack **20**, an electrochemical cell **22**, a valve **24**, a purge gas reservoir **26**, a purge gas flow regulator **28**, a power converter **30**, and a controller **32**.

The first reservoir **12** has an exterior reservoir wall **34** and contains a first solution (e.g., a vanadium anolyte) within an interior reservoir cavity **36**, where the first solution has a first reversible reduction-oxidation ("redox") couple reactant (e.g., V^{2+} and/or V^{3+} ions). The second reservoir **14** has an exterior reservoir wall **38** and contains a second solution (e.g., a vanadium catholyte) within an interior reservoir cavity **40**, where the second solution has a second reversible redox couple reactant (e.g., V^{4+} and/or V^{5+} ions).

The first and second solution flow circuits **16** and **18** each include a source conduit **42**, **44**, a return conduit **46**, **48** and a solution flow regulator **50**, **52**, respectively. The solution flow regulator **50**, **52** may include a variable speed pump connected, for example, inline within the source conduit **42**, **44**.

The flow battery stack **20** includes one or more flow battery cells **54**.

FIG. **2** illustrates a cross-section of one of the flow battery cells **54** shown in FIG. **1**. Each flow battery cell **54** includes a first current collector **56**, a second current collector **58**, a liquid-porous first electrode layer **60**, a liquid-porous second electrode layer **62**, and a separator **64** between the first and second electrode layers **60** and **62**. The first electrode layer **60** may be an anode, and the second electrode layer **62** may be a cathode. The separator **64** may be an ion-exchange membrane (e.g., a Nafion® polymer membrane manufactured by DuPont of Wilmington, Del., United States). The electrode layers **60** and **62** are positioned between the first and second current collectors **56** and **58**. Additional examples of flow battery cells are disclosed in PCT/US09/68681, and U.S. patent application Ser. Nos. 13/084,156 and 13/023,101, each of which is incorporated by reference in its entirety.

Referring to FIGS. **1** and **2**, the source conduit **42** fluidly connects the first reservoir **12** to the flow battery stack **20** such that the first current collector **56** and/or the first electrode layer **60** in each flow battery cell **54** receives the first solution. The return conduit **46** reciprocally connects the flow battery stack **20** to the first reservoir **12** such that the first reservoir **12** receives the first solution from the first current collector **56** and/or the first electrode layer **60** in each flow battery cell **54**. The source conduit **44** fluidly connects the second reservoir **14** to the flow battery stack **20** such that the second current collector **58** and/or the second electrode layer **62** in each flow battery cell **54** receives the second solution. The return conduit **48** reciprocally connects the flow battery stack **20** to the second reservoir **14** such that the second reservoir **14** receives the second solution from the second current collector **58** and/or the second electrode layer **62** in each flow battery cell **54**.

Referring to FIG. **1**, the electrochemical cell **22** may be configured as a hydrogen sensor. The electrochemical cell **22** includes a gas-porous first electrode layer **65**, a gas-porous second electrode layer **66**, a separator **68**, and a current sensor **70**. The first electrode layer **65** may be an anode, and the second electrode layer **66** may be a cathode. The separator **68** may be a proton-exchange or anion exchange electrolyte layer. The separator **68** is configured between the first and second electrode layers **65** and **66** such that the electrode layers **65** and **66** and the separator **68** may form a fuel cell **72**. Other examples of a fuel cell are disclosed in U.S. Pat. Nos. 5,156,929 and 6,617,068, each of which is hereby incorporated by reference in its entirety. The current sensor **70** is electrically connected between the first and second electrode layers **65** and **66**.

The valve **24** may be a one-way check valve. The valve **24** fluidly connects the first reservoir **12** to the electrochemical cell **22** and, in particular, a top region of the interior reservoir cavity **36** to the first electrode layer **65**. The first electrode layer **65** therefore is located outside of the exterior reservoir wall **34** in the embodiment shown in FIG. **1**.

The purge gas reservoir **26** contains purge gas such as, for example, nitrogen (N_2) gas. Other examples of purge gas include inert gases such as carbon dioxide (CO_2) gas, Argon gas, etc.

The purge gas flow regulator **28** may include a variable speed pump or an electronically actuated valve (e.g., a one-

way valve). The purge gas flow regulator **28** fluidly connects the purge gas reservoir **26** to the first reservoir **12**.

The power converter **30** may include a two-way power converter or a pair of one-way power converters. The power converter **30** may be configured as, for example, a two-way power inverter or a two-way DC/DC converter connected to a DC bus (not shown). The power converter **30** is electrically connected to the flow battery stack **20**. For example, the power converter **30** may be electrically connected to the first and second current collectors **56** and **58**.

The controller **32** may be implemented using hardware, software, or a combination thereof. The hardware may include, for example, one or more processors, a memory, analog and/or digital circuitry, etc. The controller **32** is in signal communication (e.g., hardwired or wirelessly connected) with the flow regulators **50** and **52**, the current sensor **70**, the purge gas flow regulator **28** and the power converter **30**.

The flow battery system **10** may be operated in an energy storage mode to store energy in the first and second solutions, or in an energy discharge mode to discharge energy from the first and second solutions. During both modes of operation, the controller **32** signals the solution flow regulator **50** to circulate the first solution between the first reservoir **12** and the flow battery stack **20** through the first solution flow circuit **16**. The controller **32** signals the solution flow regulator **52** to circulate the second solution between the second reservoir **14** and the flow battery stack **20** through the second solution flow circuit **18**. The controller **32** also signals the power converter **30** to exchange electrical current with (e.g., provide electrical current to, or receive electrical current from) the flow battery stack **20** and, thus, the flow battery cells **54** at a rate that corresponds to a selected current density within the cells **54**. The term "current density" describes a ratio of (i) total current delivered to or drawn from the flow battery stack **20** to (ii) an active area (not shown) of one of the flow battery cells **54**, and in particular, of the separator **64** (see FIG. **2**). Alternatively, the electrical energy may be exchanged such that there is a substantially constant exchange of power between the power converter **30** and the flow battery stack **20**, or the voltage of the power converter may be held constant. Or, any combination of galvanostatic, potentiostatic, or constant power modes may be utilized.

During the energy storage mode of operation, the electrical energy provided to the flow battery stack **20** from the power converter **30** is converted to chemical energy. The conversion process occurs through electrochemical reactions in the first solution and the second solution, and a transfer of non-redox couple reactants (e.g., H^+ ions) from the first solution to the second solution across each of the flow battery cells **54** and, in particular, each of the separators **64**. The chemical energy is then stored in the first and second solutions, which are respectively stored in the first and second reservoirs **12** and **14**. During the energy discharge mode of operation, the chemical energy stored in the first and second solutions is converted back to electrical current through reverse electrochemical reactions in the first solution and the second solution, and the transfer of the non-redox couple reactants from the second solution to the first solution across each of the flow battery cells **54**. The electrical current is then provided to the power converter **30** from the flow battery stack **20**.

Hydrogen evolution may occur within the first solution during the energy storage mode of operation when, for example, the first solution has reached an especially high state of charge (e.g., greater than approximately 90% of the V^{+3} ions have been converted to V^{+2} ions). The term "hydrogen evolution" describes a secondary reaction to the desired

energy storage process where positively charged hydrogen ions combine with negatively charged electrons. For example, instead of the desired energy storage reaction ($2V^{+3}+2e^-\rightarrow 2V^{+2}$) occurring, the following secondary hydrogen evolution reaction occurs: $2H^++2e^-\rightarrow H_2$. The electrons are produced by the reaction in the second solution (e.g., $2V^{+4}\rightarrow 2V^{+5}+2e^-$). Disadvantageously, the formation of hydrogen within the first solution may decrease system efficiency since the electrical energy is not converted into stored chemicals (i.e., the redox couples). Additionally, the secondary reaction can result in an imbalance between the states of charge of the first solution and the second solution.

FIG. **3** illustrates a method for charging the flow battery system **10** in a manner that mitigates hydrogen evolution. For ease of explanation, the following description begins with an assumption that (i) the state of charge of the first solution is less than approximately 80%, and/or (ii) little or no hydrogen evolution is occurring within the first solution. Referring to FIGS. **1** and **3**, in step **300**, the controller **32** signals the power converter **30** to provide electrical power (e.g., constant current) to the flow battery stack **20** such that the flow battery cells **54** are operated at a first energy input rate. The electrical power may be controlled at a substantially constant current, power, and/or voltage.

In step **302**, the controller **32** signals the purge gas flow regulator **28** to provide purge gas to the first reservoir **12**. The injected purge gas creates a positive pressure within the first reservoir **12** such that the purge gas and other gases within the first reservoir **12** flow through the valve **24** and into the first electrode **65**. The positive pressure as well as the valve **24** reduce/prevent a backflow of gas (e.g., air) from entering the first reservoir **12** from the electrochemical cell **22**. In an alternative embodiment, step **302** may be omitted where overpressure created by the evolution of hydrogen pushes gases within the first reservoir **12** through the valve **24** and into the first electrode **65**.

In step **304**, reactant (e.g., air) is provided to the second electrode **66**. The reactant may be provided via an electronically actuated reactant regulator (not shown), or by diffusion where the second electrode is simply exposed to ambient air.

Hydrogen may form within the first solution through hydrogen evolution when, for example, the first solution has reached a relative high (e.g., >80-90%) state of charge. In step **306**, the electrochemical cell **22**, which may be operated with a relatively low potential (e.g., 0.2 volts) and/or a relatively low resistance across the electrodes **65** and **66**, generates an electrical current when hydrogen formed by hydrogen evolution is provided to the first electrode **65** along with the purge gas. The electrical current is generated through electrochemical reactions on either side of the separator **68**, as in a fuel cell **72**.

In step **308**, the current sensor **70** senses the electrical current generated by the electrochemical reaction between the hydrogen and the reactant, and provides a current signal indicative of the sensed electrical current to the controller **32**.

In step **310**, the controller **32** processes the current signal, and provides a control signal to the power converter **30**. The current signal may be processed, for example, by comparing a value of the current signal to one or more threshold values. Each threshold value is indicative of a predetermined current signal value.

FIG. **4** is a graphical illustration of (i) a first curve **400** showing the sensed electrical current versus time, and (ii) a second curve **402** showing electrical potential (vs. a hydrogen reference electrode) of the first solution versus time. An example of a threshold value is shown at time t_{33} where the sensed electrical current becomes greater than zero, which

corresponds to when hydrogen begins to form within the first solution. Another threshold value is shown at time t_{36} (e.g., where the sensed electrical current is equal to approximately 1.8 amps), which corresponds to when the first solution becomes overcharged (i.e., reaches approximately 100% state of charge). This is also where the electrical potential of first solution levels off because the side reaction (hydrogen evolution) begins consuming substantially all of the current, which is not desirable and is why a method to detect this condition before it occurs is advantageous. FIG. 4 therefore illustrates how the electrochemical cell 22 may detect hydrogen evolution before, for example, it becomes excessive.

The detection of hydrogen evolution within the first solution does not depend on which flow battery cell, or cells, in the flow battery stack are generating hydrogen since the first solution (with hydrogen, if generated) returns to the first reservoir 12. Whereas if one tries to use the flow-battery cell potential, one would need to measure the cell voltages of each of the individual cells, as well as measure the half-cell potentials using a reference electrode. Such a method, however, requires a lot of instrumentation and data collection. The control signal is provided to the power converter 30 to control the exchange of electrical power between the power converter 30 and the flow battery cells 54 as a function of the electrical current generated by the electrochemical cell 22. For example, where the current signal value is greater than or equal to one or more of the threshold values, the control signal may be used to (i) iteratively or continuously reduce power (e.g., the current density) within the flow battery cells 54, or (ii) stop the exchange of electrical power between the power converter 30 and the flow battery cells 54. The current density may be reduced, for example, to a predetermined level that corresponds to a respective one of the thresholds met by the current signal value. Alternatively, the current density may be reduced as a function of the electrical current being generated by the electrochemical cell 22 such that as the current signal value increases, the current density decreases.

The formation of hydrogen within the first solution due to hydrogen evolution may be mitigated using the aforesaid method. For example, when the current sensor 70 initially senses an electrical current caused by an electrochemical reaction between the hydrogen and the reactant, the controller 32 may signal the power converter 30 to stop providing electrical current to the flow battery stack 20 to prevent additional formation of hydrogen. In another example, when the current sensor 70 initially senses the electrical current, the controller 32 may signal the power converter 30 to reduce the electrical current being provided to the flow battery stack 20 to reduce the hydrogen evolution rate. However, once the current signal value is greater than or equal to a specified threshold value (e.g., where the rate of hydrogen production is considered to be excessive), the controller 32 may signal the power converter 30 to stop providing electrical current to the flow battery stack 20 to prevent the first solution from becoming overcharged and thus from generating excessive hydrogen. The aforesaid method may also improve the safety of the flow battery system 10 by consuming the hydrogen gas produced by hydrogen evolution through the electrochemical reaction within the electrochemical cell 22.

In some embodiments, the controller 32 may additionally or alternatively process the sensed current signal to determine how much hydrogen is being formed within the first solution using Faraday's Law. The hydrogen that is consumed in the first electrode 65, for example, is equal to I/2F, where I is the current sensed by the sensor 70 and F is Faraday constant (96,485 coulombs/mol).

FIG. 5 illustrates an alternative embodiment of a flow battery system 510. In contrast to the flow battery system 10 shown in FIG. 1, the first electrode 65 is located within the exterior reservoir wall 34, while the second electrode 66 remains located outside of the exterior reservoir wall 34. This configuration may reduce the complexity of the system since, for example, the valve 24 may be omitted. The purge gas reservoir 26 may also be omitted since the likelihood of air entering the first electrode 65 and flowing into the first reservoir 12 is greatly reduced as the first electrode 65 is sealed within the first reservoir 12. The electrodes 65 and 66 and the separator 68 may also be designed and configured in such a way to ensure that most of the water produced drains back to the first reservoir 36, if desired.

While various embodiments of the flow battery system have been disclosed, it will be apparent to those of ordinary skill in the art that many more embodiments and implementations are possible within the scope of the flow battery system. Accordingly, the present flow battery system is not to be restricted except in light of the attached claims and their equivalents.

What is claimed is:

1. A flow battery system, comprising:
    a first reservoir containing a first solution comprising a first reversible redox couple reactant;
    a plurality of flow battery cells that receive the first solution;
    a hydrogen sensor connected to and in fluid communication with the first reservoir, wherein the hydrogen sensor is configured to receive gas from a top region of a cavity of the first reservoir; and
    a power converter that exchanges electrical power with the flow battery cells as a function of a current signal provided by the hydrogen sensor.

2. The system of claim 1, wherein the hydrogen sensor comprises an electrochemical cell that comprises
    a first electrode that receives hydrogen from the first reservoir;
    a second electrode that receives reactant; and
    a current sensor that senses electrical current generated within the electrochemical cell by an electrochemical reaction between the hydrogen and the reactant, and provides the current signal indicative of the sensed electrical current.

3. The system of claim 2, wherein the electrochemical cell further comprises one of a proton exchange electrolyte layer and an anion exchange electrolyte layer that separates the first electrode from the second electrode.

4. The system of claim 2, wherein:
    the first solution comprises an anolyte;
    the first electrode comprises an anode; and
    the second electrode comprises a cathode.

5. The system of claim 2, wherein the reactant comprises air.

6. The system of claim 2, wherein the first electrode is located outside of the first reservoir.

7. The system of claim 6, wherein the first electrode is fluidly connected to the first reservoir through a one-way valve.

8. The system of claim 6, wherein the first reservoir receives purge gas such that the hydrogen within the first reservoir flows to the first electrode.

9. The system of claim 2, wherein
    the first electrode is located within an exterior reservoir wall of the first reservoir; and
    the second electrode is located outside the exterior reservoir wall of the first reservoir.

10. The system of claim **1**, further comprising a controller that receives the current signal and provides a control signal to the power converter to control a rate at which the power converter exchanges electrical power with the flow battery cells.

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